

СВОЙСТВА ДИНАМИЧЕСКИХ ТЕРМОЭЛАСТОПЛАСТОВ НА ОСНОВЕ ПОЛИПРОПИЛЕНА И БУТАДИЕН-НИТРИЛЬНОГО КАУЧУКА

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Приводятся результаты исследования влияния концентрации различных марок бутадиен-нитрильного каучука, типа и содержания сшивающего агента на физико-механические и термомеханические свойства полимерных композиций на основе полипропилена. Смешение компонентов смеси осуществляли на горячих вальцах в режиме расплава при температуре 170 °С. Предварительное исследование влияния концентрации каучука на свойства композиций на основе полипропилена показало, что введение эластомерного компонента приводит к закономерному снижению прочности и относительного удлинения композиций. Результаты исследования термомеханических свойств полимерных композиций показали, что при концентрации каучука 30 % масс. и выше на термомеханических кривых заметно выделяется область высокоэластического состояния, характерного для резин. Принимая во внимание, что резиновые материалы получают в процессе их вулканизации, представлялось интересным для получения сопоставимых результатов провести сшивку материалов двумя типами вулканизирующих агентов - пероксидом дикумила и серы. Концентрацию пероксида дикумила варьировали в пределах 0,5 – 2,0% масс. Установлено, что использование пероксида дикумила в количестве 1,0-2,0% масс. сопровождается интенсивным протеканием сшивки с образованием в полимерной композиции необратимой густосетчатой структуры. По результатам оценки показателя текучести расплава вулканизованных композиций было найдено, что при концентрации пероксида дикумила в количестве 0,5% масс. они еще сохраняют способность к течению. При концентрациях пероксида дикумила свыше 0,5% масс. полимерные композиции полностью теряют текучесть расплава. Было установлено, что с увеличением концентрации серы от 3,0 до 10% масс. наблюдается снижение показателя текучести расплава от 2,76 до 0,616 г/10 мин. Было найдено, что процесс сшивки преимущественно протекает по двойным связям СКН, способствующим, тем самым, получению динамически вулканизованных полимерных материалов с уникальным сочетанием структуры и свойств. Подтверждением сказанному были результаты исследования термомеханических характеристик композиций, согласно которым во всех образцах, подвергнутых серной вулканизации, наблюдается переход из области высокоэластического состояния в вязкотекучее. Результаты исследования позволяют утверждать о том, что динамические термоэластопласты возможно получить только при правильном подборе соотношения используемых компонентов в полимерной композиции.

Ключевые слова: полипропилен, бутадиен-нитрильный каучук, агент вулканизации, дикумил пероксид, сера, термо-деформационные характеристики

PROPERTIES OF DYNAMIC THERMOPLASTIC ELASTOMERS BASED ON POLYPROPYLENE AND BUTADIEN-NITRIL RUBBER

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The study results of the influence of butadiene-nitrile rubber different grades concentration, cross-linking agent type and content on the physico-mechanical and thermo-deformation properties of polymer compositions based on polypropylene are presented. Mixing of the components was carried out on hot rollers in the melt mode at 170 °C. A preliminary study of rubber concentration affect on the properties of compositions based on polypropylene showed that the introduction of an elastomeric component leads to a regular decrease in the strength and elongation at break of the compositions. The results of investigation of the thermo-deformation properties of polymer compositions showed that at a rubber concentration of 30wt%, and higher on thermomechanical curves, the region of the high-elastic state characteristic of rubbers is noticeably distinguished. Taking into account that the rubber materials are obtained during the process of their vulcanization, it seemed interesting to crosslink materials with two types of vulcanizing agents – dicumyl peroxide and sulphur for obtaining comparable results. The concentration of dicumyl peroxide was varied between 0.5 - 2.0 wt%. It was found that the use of dicumyl peroxide in an amount of 1.0-2.0 wt% is accompanied by intense occurrence of crosslinking with the formation of an irreversible highly crosslinked structure in the polymer composition. Based on the evaluation of the melt flow index of the vulcanized compositions, it was found that at the concentration of dicumyl peroxide in an amount of 0.5 wt% they still retain the ability to flow. At concentrations above 0.5 wt% of dicumyl peroxide the polymer compositions completely lose the fluidity of the melt. It was found that with an increase in the sulphur concentration from 3.0 to 10 wt% the decrease in the melt flow index from 2.76 to 0.616 g/10 min is observed. It was found that the crosslinking process predominantly proceeds through double bonds of butadiene-nitrile rubber, thereby facilitating the production of dynamically vulcanized polymer materials with a unique combination of structure and properties. This was confirmed by the results of a study of the thermo-deformation characteristics of compositions, according to which a transition from the region of a high-elastic state to viscous-flow state is observed in all samples subjected to sulfur vulcanization. The results of the study make it possible to state that dynamic thermoplastic elastomers can be obtained only if the ratio of the components used in the polymer composition is correctly selected.

Key words: polypropylene, butadiene-nitrile rubber, vulcanizing agent, dicumyl peroxide, sulphur, thermo-deformation characteristics

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INTRODUCTION

Polymer materials are widely used in various fields of technology. This, first of all, is due to sufficiently good physical and mechanical properties and the ability to be processed into various structural types of products within a few seconds. As technology progresses in such profiling areas as engineering, shipbuilding, aircraft construction, and in key areas such as space, military and military space equipment, ever more stringent requirements have been made towards the quality of polymer materials used in these areas. Of particular interest are polymer materials such as thermoplastic elastomers, which are known to have the properties of rubbers, but are processed as conventional thermoplastics. A great interest in these materials is due to the fact that for the production of rubber products in the pressing process it takes 20-30 min, while for the production of similar products of thermoplastic elastomers it takes no more than one minute [1-5].

Thermoplastic elastomers are materials obtained by mixing thermoplastics with elastomers. Despite the obvious advantages of thermoplastic elastomers in their manufacture, there are problems associated with the compatibility of the blended components of the mixture. This problem becomes even more urgent when polar polymers are used as blended polymers. In particular, we are talking about non-polar polyolefins and polar synthetic elastomers. In the absence of sufficient technological compatibility between them, polymer materials obtained on their basis are characterized by low physical and mechanical characteristics that are inadmissible for the manufacture of qualitative structural products on their basis. In this regard, various methods are being adopted to improve the technological compatibility of polymer mixtures by introducing into their composition various modifiers, compatibilizers, structurants, plasticizers, etc. [6-8].

In this regard, the aim of the studies was to solve two main problems, using polypropylene (PP) and butadiene-nitrile rubber (SKN) as examples: improving the technological compatibility of the polymers of different polarity and obtaining thermoplastic elastomers based on them.

EXPERIMENTAL PART

Polypropylene (PP), butadiene-nitrile rubber grade SKN-18, SKN-26 and SKN-40 were used as the object of the study. The concentration of SKN in the composition based on PP was changed in the range of 0-50 wt%.

Dicumyl peroxide (PD) – a light yellow powder, with $T_m = 40$ °C, is intended for the preparation of crosslinked structures in polymers.

In order to improve the miscibility and technological compatibility of SKN with PP compatibilizer has been used, which is the methacrylic acid-modified PP (PPMAA).

The compatibilizer was produced in the process of mechanochemical synthesis of the modified PP. For this purpose, MAA was injected into the PP melt at the temperature of 180-190 °C. As a result of intensive thermomechanical effect in PP melt macroradicals are formed which joined MAA monomers. The concentration of MAA in the composition of the PP was determined according to the method of IR spectral analysis developed by us earlier using the calibration formula $C = 23.1D$ [8]. According to the calibration formula, the concentration of MAA in the compatibilizer (PPMAA) was 38 wt%.

Mixing of polymer blends was carried out on friction rollers at the temperature of 150-160 °C, and the rolling time of 10 min. After melting of the PP at the beginning PMAA was introduced in an amount of 3-7 wt%, further SKN was introduced and mixed for 7 min. In order to vulcanize the polymer blends, the crosslinking agent - dicumyl peroxide (DP) in the amount of 0.5-2.0 wt% or sulfur in the range of 3-10 wt% was added to the composition on the rollers. Pressing of plates for testing the physico-mechanical properties of composite materials was carried out at the temperature of 170-180 °C.

The melt flow index (MFR) of the polymer compositions was determined on rheometer "MELT FLOW TESTER CEAST MF50" (INSTRON, Italy) at 190 °C and the load of 5 kg.

Physico-mechanical characteristics were determined by standard methods: tensile yield stress (σ_t) and elongation at break (ϵ) were determined in accordance with GOST 11262-80.

The gel fraction was determined in Soxhlet apparatus, where xylene was used as solvent for PP and SKN.

Thermomechanical properties were determined on the Kanavets plastometer. The deformation was measured at successively varying temperatures. When constructing a thermomechanical curve of a polymer, it is very important to cover, if possible, the entire temperature range of the polymer composition – glassy (crystalline), high-elastic and viscous-flow state. Thermomechanical curves reflect all possible physical, physico-chemical and chemical processes occurring in the sample as a result of change in the temperature of the experiment and, thereby, provide reliable information on the temperature transitions that are significant for polymer processing.

RESULTS AND DISCUSSION

For a better understanding of the processes occurring in the formation of thermoplastic elastomers, as the object of the study were chosen polymer systems such as PP+SKN-40, PP+SKN-26, PP+SKN-18. The use of a wide range of components of the mixture makes it possible to obtain reliable information on the effect of the composition, type, and concentration of the reacting components of the polymer composition on their thermal deformation and physico-mechanical properties on the basis of a system analysis of the experimental data. Table 1 shows the deformation-strength properties of the above mentioned polymer mixtures without any modifying additives. It was necessary to find out how the deformation-strength properties of polymer mixtures based on PP change depending on the content of SKN of different grades in the composition.

Analyzing the data presented in Table 1, it can be established that the introduction of SKN into the composition of PP leads to a deterioration in the deformation-strength characteristics of polymer mixtures. Such decrease in strength is characteristic for polymer compositions in which an elastomeric component is introduced. Polymer mixtures of thermoplastic with an

elastomer, as a rule, lead to the formation of the structure and properties of thermoplastic elastomers. In this case, the properties of the samples were characterized by the tensile yield stress (σ_t , MPa) and elongation at break (ε , %), which are most sensitive to changes in the structure and formulation of compositions. As can be seen from Table 1, irrespective of the SKN grade, significant decrease in ε of polymer mixtures is observed simultaneously with the decrease of σ_t : from 550% for the initial PP to 10-20% for the PP mixture + 50 wt% SKN. On the one hand, the introduction of an amorphous component to 50 wt% in the composition of semicrystalline PP leads to decrease in the degree of crystallinity from 58 to 12%, and on the other hand, such sharp decrease in the strength and elongation at break of the polymer mixtures under consideration unequivocally testifies to the lack of necessary technological compatibility and sufficient miscibility of these polymers.

As can be seen from Table-1, the samples containing in their composition as the elastomeric component SKN-18 are characterized by comparatively better values for strength and relative elongation.

Table 1

Influence of the concentration of different SKN grades on the tensile yield stress and elongation at break (σ_t/ε) of composite materials based on PP

Таблица 1. Влияние концентрации различных марок СКН на предел текучести при растяжении и относительное удлинение (σ_t/ε) композиционных материалов на основе ПП

№	Composition formulation	Concentration of SKN in the composition of PP, wt%					
		0	10	20	30	40	50
1	PP+SKN-18	33.6/250	25.8/150	18.4/90	9.3/45	5.4/20	3.8/10
2	PP+SKN-26	33.6/250	25.0/140	16.7/80	8.8/30	5.2/20	3.8/10
3	PP+SKN-40	33.6/250	22.2/120	13.5/55	7.2/10	4.3/10	3.2/10

The relatively low polarity of this rubber provides a relatively better compatibility with nonpolar PP. As the concentration of nitrile groups in the composition of SKN increases (from 18 to 40 wt%), its technological compatibility with PP significantly deteriorates, which is manifested in significant decrease in deformation-strength characteristics.

In order to improve the compatibility of the considered components of the mixture methacrylic acid-modified PP has been used as compatibilizer. Modification of PP by the above mentioned acrylic monomer was carried out during its introduction into the hot melt of PP in roll mills. The compatibilizer obtained in the process of mechanochemical synthesis was characterized by the presence of hydrocarbon macrochains of PP and grafted MAA chains. Actually, one of the main features of the compatibilizer structure

is that one branch of the macro chain combines with the nonpolar one and the other with the polar polymeric component. In this case, apparently, the free hydrocarbon part is built into the crystal structure of the PP, and the grafted MAA chains are distributed in the SKN phase or in the regions bordering it. Such interaction of the multi-polar macrochains helps to reduce the interfacial tension and increase adhesion at the interface between the polymer phases. We assume that this type of compatibilizers is mainly distributed in the boundary regions of the interphase region, which, like filaments, bind two dissimilar polymers [5, 9].

To confirm what was said, the results of study of the effect of the concentration of SKN and compatibilizer (PPMAA) on the tensile yield stress and the elongation at break of the compositions are presented

in Table 2. The concentration of MAA in the composition of PP was 38 wt%. From the experimental data, it can be established that, in concentration-dependent PPMAC, the strength and elongation at break are changed according to particular regularity. Firstly, the introduction of PPMAC in the composition of the initial PP leads to a change in the tensile yield stress with a maximum at its concentration equal to 5.0 wt%. It is typical that with an increase in the concentration of

PPMAA elongation at break is constantly decreasing, which may be due to its incompatibility with the polymer matrix (PP). The fact that the maximum strength of the compositions is achieved when 5.0 wt% PPMAA can be interpreted by the fact that during the crystallization process of PP melt macrochain segments containing polar groups, preferably displaced in amorphous region and crystal defects.

Table 2

Influence of the concentration of various SKN grades on the tensile yield stress / elongation at break (σ_t/ϵ) of composite materials based on PP, modified with a compatibilizer (PPMAA)

Таблица 2. Влияние концентрации различных марок СКН на предел текучести при растяжении/относительное удлинение (σ_t/ϵ) композиционных материалов на основе ПП, модифицированных компатибилизатором (ППМАК)

№	Composition formulation	Concentration of SKN in the composition of PP, wt%					
		0	10	20	30	40	50
1	PP+SKN-18+3.0% Ct	30.3/185	26.4/190	18.9/145	9.9/115	5.8/90	4.0/50
2	PP+SKN-26+3.0% Ct	30.3/185	25.8/190	17.5/135	9.2/100	5.5/70	4.0/60
3	PP+SKN-40+3.0% Ct	30.3/185	24.5/190	14.4/115	8.7/85	5.1/50	3.7/50
4	PP+SKN-18+5.0% Ct	28.8/155	26.9/175	19.1/155	10.2/110	6.2/100	4.2/90
5	PP+SKN-26+5.0% Ct	28.8/155	27.4/180	18.2/160	9.7/95	5.7/90	4.5/75
6	PP+SKN-40+5.0% Ct	28.8/135	25.7/175	16.6/150	9.3/65	6.5/80	4.4/60
7	PP+SKN-18+7.0% Ct	27.5/130	26.0/145	18.2/110	9.1/95	5.7/70	3.2/40
8	PP+SKN-26+7.0% Ct	27.5/130	28.0/165	19.0/120	10.4/85	6.3/50	4.9/45
9	PP+SKN-40+7.0% Ct	27.5/130	26.3/160	17.8/95	9.8/65	6.9/40	5.7/45
10	PP+SKN-18+10.0% Ct	24.9/55	24.4/85	16.3/85	7.2/65	3.8/55	2.7/30
11	PP+SKN-26+10.0% Ct	24.9/55	26.1/90	18.1/80	8.8/50	5.1/35	3.7/30
12	PP+SKN-40+10.0% Ct	24.9/55	25.8/95	16.0/75	9.2/45	6.2/30	4.3/20

*compatibilizer – in the table abbreviated Ct

* компатибилизатор обозначается Ct

We believe that the concentration of polar groups in amorphous regions that have a large number of "pass-through" chains leads first to the strengthening of the supramolecular structure of the polymer matrix. Introduction of more than 5wt% PPMAA, on the contrary, already leads to decrease in the σ_t of the initial PP. The latter circumstance is interpreted by the fact that at high concentrations of polar groups in amorphous PP regions, the latter block the segmental mobility of the transmission chains, thereby contributing to brittle fracture of the sample [5, 9].

The introduction of compatibilizer in the composition PP+SKN, regardless of the SKN grade and its concentration in the composition, significantly improves the deformation-strength characteristics. In this case, the more nitrile groups content in SKN, the effect of improving σ_t and ϵ of PP + SKN composition is observed at higher concentrations of PPMAC. In other words, the greater the polarity of the synthetic rubber, the more the compatibilizer is required to achieve the maximum effect in properties.

It is quite obvious that SKN is vulcanized by sulphur and organic peroxides. This issue in the literature is given a lot of attention. However, in spite of this, studies dealing with the production of dynamically vulcanized thermoplastic elastomers based on a mixture of PP+SKN+PPMAA are very limited. Therefore, in this paper we made an attempt to separately consider the possibility of vulcanization of PP+SKN compositions with dicumyl peroxide (DP) and sulphur in the presence of PP-MAA. It was important to find out how essential the role of the compatibilizer in the process of vulcanization and the formation of the region of high-elastic deformation, characteristic for rubbers.

Table 3 presents the results of a study of the influence of the various grades of SKN and DP concentration on the stress-strain properties of composites based on PP+SKN+PPMAA. From the comparative analysis of the data given in this table, it can be established that with an increase in the concentration of DP from 0.5 to 2.0 wt%, there is a regular tendency to decrease the strength of the initial PP modified with compatibilizer. This circumstance is interpreted in that the

introduction of DP into the PP melt promotes the formation of macroradicals of the initial PP and compatibilizer, which in the process of recombination lead to the formation of an irreversible cross-linked spatial structure. In the process of crystallization from the melt, the crosslinked sections exert a substantial counteraction to the formation of long-range order in the crystalline phase of the PP. Therefore, in the process of crystallization from melt in such structures, the growth of crystals is accompanied by the displacement and concentration of crosslinked and unordered branches in the interspherulite space. And, the greater the concentration of DP in the composition, the more cross bonds are formed, which hinders crystallization from the melt. The results of the study of crosslinked compositions properties are confirmation of this. Firstly, it is necessary to single out common patterns in changing properties and, secondly, to substantiate the main reasons that contribute to these changes. Thus, for example, with an increase in the concentration of the elastomeric component, there is a general tendency to decrease the strength and increase in the elongation at break, which is typical for this type of polymer mixtures. At the same concentration of the elastomeric component with an increase in the content of nitrile

groups in the SKN (SKN-18 → SKN-26 → SKN-40), the strength and elongation of the compositions are regularly decreased. This is interpreted by the fact that, as already noted above, the PP is poorly combined with the polar nitrile rubber and, the more nitrile groups in the SKN, the greater the polarity of the rubber and, accordingly, the worse with their technological compatibility. From a comparative analysis of the data in Table 3, it can be established that compositions with 0.5 wt% of DP possess relatively high stress-strain properties. We assume that at small concentrations of DP the crosslinking proceeds predominantly along the most vulnerable double bonds of the SKN, as a result of which dynamically vulcanized thermoplastic elastomers are formed [10,11]. In other words, these results in obtaining a rare network structure with a unique morphology in which the cured elastomer particles (SKN) are dispersed in the continuous phase of the thermoplastic matrix. At high concentrations of DP, highly cross-linked spatial structure is formed throughout the volume of the composition with the participation of macrochains not only of elastomers but also of PP. Therefore, in order to obtain dynamically vulcanized thermoplastic elastomers, it is necessary to use DP with its minimum content (up to 0.5 wt %).

Table 3

Influence of the concentration of various SKN grades and crosslinking agent (DP) on the tensile yield stress/elongation at break (σ_t/ϵ) of composite materials based on PP, modified with 5 wt% PPMAA

Таблица 3. Влияние концентрации различных марок СКН и сшивающего агента (ПД) на предел текучести при растяжении/относительное удлинение (σ_t/ϵ) композиционных материалов на основе ПП, модифицированных 5% масс. ППМАК

№	Composition formulation	Concentration of SKN in the composition of PP, wt%					
		0	10	20	30	40	50
1	PP+SKN-18+5.0% Ct+0.5DP	32.5/95	28.5/100	20.3/125	12.1/165	7.2/190	5.3/210
2	PP+SKN-26+5.0% Ct+0.5DP	32.5/95	29.1/110	21.5/130	12.8/170	7.4/205	5.9/190
3	PP+SKN-40+5.0% Ct+0.5DP	32.5/95	27.8/105	19.5/120	10.9/155	7.9/100	5.8/90
4	PP+SKN-18+5.0% Ct+1.0DP	25.4/60	28.2/90	21.2/135	13.7/150	8.4/165	6.1/190
5	PP+SKN-26+5.0% Ct+1.0DP	25.4/60	28.8/80	22.4/130	13.2/155	8.7/175	6.2/175
6	PP+SKN-40+5.0% Ct+1.0DP	25.4/60	26.0/70	19.8/110	11.5/125	8.8/90	6.2/80
7	PP+SKN-18+5.0% Ct+2.0DP	17.7/15	18.0/35	18.2/50	11.1/75	7.7/90	6.3/90
8	PP+SKN-26+5.0% Ct+2.0DP	17.7/15	18.4/25	17.7/40	12.5/75	8.6/80	6.5/85
9	PP+SKN-40+5.0% Ct+2.0DP	17.7/15	18.0/20	16.8/40	10.6/65	7.7/70	7.0/75

*compatibilizer – in the table abbreviated Ct

* компатибилизатор обозначается Ct

If we compare the data in Table 2 and 3, it can be established that in the crosslinked compositions (PP + SKN) elongation at break and strength are higher than those for unvulcanized ones. With increasing concentration of the elastomeric component, the crosslinking promotes in a greater degree the appearance of rubber properties in the samples. The latter circumstance is expressed in significant increase in the elongation at break of the samples. At a relatively higher

concentration of DP, equal to 2.0 wt% highly cross-linked spatial structure is formed in the samples. The last impairs deformation-strength properties of composite materials.

Table 4 shows the results of the study of the sulphur vulcanization effect on the regularity of the change in the deformation-strength characteristics of compositions based on PP + SKN. Analyzing the data in this table, it can be established that the introduction

of sulphur improves the deformation-strength properties of modified PP samples that do not contain an elastomeric component. Along with this, vulcanized polymer mixtures remain the properties at a satisfactory level.

In order to find out at what ratio of polymer components in the compositions the properties of thermoplastic elastomers are manifested; let us turn to the

results of investigation of their thermomechanical properties. For this purpose, the results of the investigation of the thermomechanical characteristics of unvulcanized and vulcanized polymer mixtures are given in Fig. 1-4.

Table 4

Influence of the concentration of various SKN grades and sulphur on the tensile yield stress/elongation at break (σ/ϵ) of composite materials based on PP, modified with 5 wt% PPMAA

Таблица 4. Влияние концентрации различных марок СКН и серы на предел текучести при растяжении/относительное удлинение (σ/ϵ) композиционных материалов на основе ПП, модифицированных 5% масс. ППМАК

№№	Composition formulation	Concentration of SKN in the composition of PP, wt%					
		0	10	20	30	40	50
1	PP+SKN-18+5.0% Ct+3.0% S	33.4/275	27.2/280	19.5/280	10.1/135	5.8/90	4.1/90
2	PP+SKN-26+5.0% Ct+3.0% S	33.4/275	26.3/310	17.4/250	9.5/170	5.7/205	4.2/190
3	PP+SKN-40+5.0% Ct+3.0% S	33.4/275	24.9/165	14.5/125	8.0/105	4.9/80	3.7/65
4	PP+SKN-18+5.0% Ct+5.0% S	34.7/300	27.9/490	20.4/135	10.8/150	6.2/165	4.5/190
5	PP+SKN-26+5.0% Ct+5.0% S	34.7/300	27.0/320	18.3/250	10.1/160	6.4/175	4.8/175
6	PP+SKN-40+5.0% Ct+5.0% S	34.7/300	25.8/170	15.9/150	8.5/125	5.6/100	4.4/90
7	PP+SKN-18+5.0% Ct+10.0% S	31.5/170	24.5/185	17.0/180	9.5/165	5.3/150	4.0/70
8	PP+SKN-26+5.0% Ct+10.0% S	31.5/170	25.1/170	16.1/150	8.2/155	5.5/110	3.9/85
9	PP+SKN-40+5.0% Ct+10.0% S	31.5/170	22.5/180	13.7/115	7.8/105	4.9/95	3.8/65

**compatibilizer – in the table abbreviated Ct, sulphur – S

** компатибилизатор обозначается Ct, сера - S

Thus, for example, Fig. 1 shows the results of study of the polymer mixtures PP+SKN-40 thermomechanical characteristics at various ratios. The choice of SKN-40 is justified by the fact that this grade of nitrile rubber contributes the most to the production of benzoil-heat-resistant materials operating under severe extreme operating conditions. Analyzing the presented experimental data, it can be established that the SKN-40 exerts a certain influence on the character of the change in the thermomechanical curves. At 20 wt% the latter has an insignificant effect on the regularity of the change in the thermomechanical curve. However, at the concentration of SKN-40, equal to 30 wt% and above there is a process approaching the formation of a region of high-elastic deformation.

The transition to the viscous-flow state at 30, 40, and 50 wt% of SKN-40, starts at 157, 164 and 166 °C respectively. At the same time, the process of transition from the crystalline to the high-elastic state for compositions with 30, 40, and 50 wt% SKN-40, begins at the temperature equal to 141, 143 and 135 °C, respectively. In other words, with an increase in the concentration of the elastomeric component, the sharpest temperature transition from crystalline to high-elastic occurs at the concentration of 50 wt%. At the same time, an appreciable temperature transition from the highly elastic to the viscous-flow state occurs at 40 wt% of SKN-40.

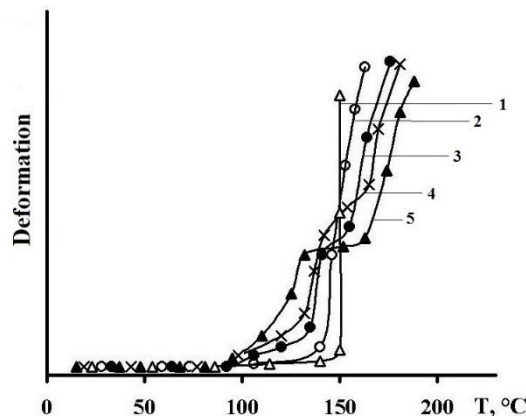


Fig. 1. Influence of the concentration of SKN-40 (wt%) on the nature of the change in thermomechanical curves of compositions based on PP + SKN-40: 1- 0; 2 - 20; 3 - 30; 4 - 40; 5 - 50

Рис. 1. Влияние концентрации СКН-40 (%масс.) на характер изменения термомеханических кривых композиций на основе ПП+СКН-40: 1- 0; 2 - 20; 3 - 30; 4 - 40; 5 - 50

In order to study the compatibility of the polymer mixtures under consideration and to reveal the role of the compatibilizer in the change in the thermomechanical curves, we consider the data presented in Fig. 2. This figure shows the thermomechanical curves of the compositions PP+SKN-40 + 5.0 wt% PPMAA with different concentrations of the elastomeric component. As can be seen from this figure, at a concentration of SKN-40 equal to 30 wt% and above, a region of high-elastic deformation begins to be traced in the composi-

tion, which, with further increase in temperature, becomes a viscous-flow state. From the comparative analysis of the data in Figs. 1 and 2, it can be established that the process of forming a region of high-elastic deformation in the presence of a compatibilizer at 30 wt% concentration of SKN-40 is less pronounced. It is also characteristic that the formation of a plateau in the region of high-elastic deformation begins most clearly at 40 wt% SKN and higher.

In this case, the transition to the viscous-flow state in compositions with 30, 40, and 50 wt% of SKN-40 begins, respectively, at 152, 154, 158 °C. In comparison with the thermomechanical curves shown in Fig. 1, the process of transition to the viscous-flow state in the presence of compatibilizer begins at relatively low temperature. The transition temperature from crystalline to high-elastic for samples with 30, 40 and 50 wt% begins respectively at the temperature of 142, 138 and 127 °C. It becomes obvious that the use of PPMAA as a compatibilizer of polymer mixtures PP+SKN-40 helps to reduce temperature transitions from one state to another. The latter circumstance favorably affects the processing of composite materials, as it helps to reduce energy costs. Thus, the influence of the compatibilizer on reducing temperature transitions from one state to another can also indicate the production of thermoplastic elastomers, which have a unique combination of rubber-like properties that are processed like conventional thermoplastics.

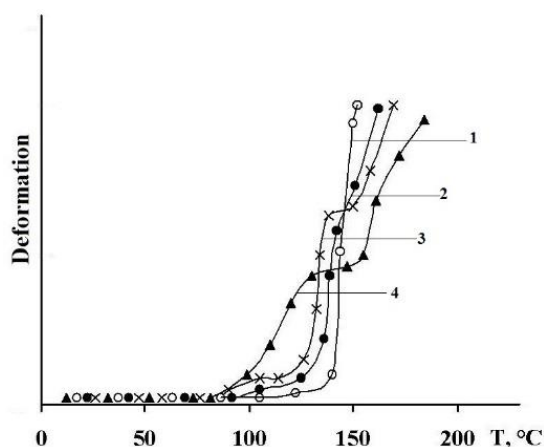


Fig. 2. Influence of the concentration of SKN-40 (wt%) on the nature of the change in thermomechanical curves of compositions based on PP+SKN-40+5 wt% PPMAA: 1-20; 2- 30; 3 -40; 4 -50
 Рис. 2. Влияние концентрации SKN-40 (% масс.) на характер изменения термомеханических кривых композиций на основе ПП+СКН-40+5% масс. ППМАА: 1-20; 2- 30; 3 -40; 4 -50

It is quite obvious that the process of properties formation of thermoplastic elastomers will depend not only on the concentration of SKN-40. Judging by the thermomechanical curves, thermoplastic elastomers

are more likely to characterize compositions containing, in addition to 5.0 wt% PPMAA, 40-50 wt% SKN-40 for the compositions in question. The obtained results unequivocally testify to the fact that PPMAA has a significant influence on the improvement of technological compatibility of the blended components and, thereby, contribute to the production of new types of thermoplastic elastomers on their basis.

Despite a sufficient number of works devoted to the problem of obtaining vulcanized thermoplastic elastomers, very limited research is devoted to the problems of studying the effect of the type and concentration of crosslinking agents on their thermomechanical characteristics [1, 6, 8]. In this connection, it seemed interesting to investigate the effect of various crosslinking agents on the nature of the change in the thermomechanical properties of polymer mixtures. At the same time, based on the results of the study of the compositions properties in question, the samples based on PP + 50 wt% SKN-40+5.0 wt% PPMAA were used as the object of the study.

For example, Fig. 3 and 4 show the results of studying the effect of DP and sulphur on the nature of the change in the thermomechanical properties of the objects under study. Comparing the curves in Fig. 3, it can be seen that with an increase in the concentration of PD from 0.5 to 2.0 wt%, there are quite significant changes in thermomechanical curves.

According to the data presented in Fig. 3, the introduction of DP into the composition is accompanied by an increase in the temperature transition from the crystalline to the high-elastic state. So, for example, as the concentration of DP increases from 0 to 2.0 wt% the initial process of deformation processes in general starts from 98 to 143 °C, respectively. The temperature transition from crystalline to high-elastic changes, respectively, in the range of 128-167 °C.

The temperature transition from the high-elastic state to the viscous flow is manifested only in samples with rare network structure, crosslinked by 0.5 wt% of DP, and is 187 °C. At the concentration of DP above 0.5 wt% there are irreversible rigid crosslinked structures that hamper the process of softening the polymer mixture. And, the more the concentration of DP introduced into the composition, the more rigid highly crosslinked structures are formed. According to the thermomechanical curves presented in Fig. 3, the addition of 0.5 wt% of DP still retains the ability of the polymer mixture to transition from a high-elastic state to viscous flow at 187 °C, enabling them to be processed by injection molding and extrusion methods. We assume that the introduction of 0.5 wt% DP creates the conditions for proceeding of the dynamic vulcanization of the rubber phase.

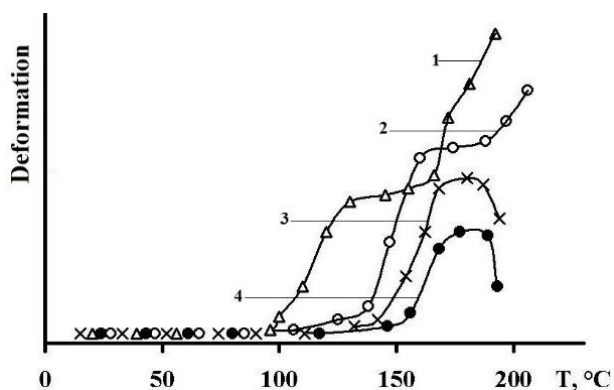


Fig. 3. Influence of the concentration of DP (wt %) on the nature of the change in thermomechanical curves of compositions based on PP+50 wt% SKN-40+5 wt% PPMAA+DP: 1- 0; 2- 0.5; 3- 1.0; 4- 2.0

Рис. 3. Влияние концентрации ПД (%масс.) на характер изменения термомеханических кривых композиций на основе ПП+50%масс. СКН-40+5%масс. ППМАА+ПД: 1- 0; 2- 0,5; 3- 1,0; 4- 2,0

Further increase in the concentration of DP (more than 0.5 wt %) leads to the fact that the sample loses its ability to transition to a viscous flow state. In this case, not only the rubber phase is crosslinked, but also the PP macromolecules, which is accompanied by a further deterioration of the properties and the ability of the compositions to deform. We do not exclude that at this temperature, due to the residues of the unreacted DP, a further process of crosslinking takes place throughout the volume of the polymer matrix, which further complicates the deformation of the samples. In this state, the crosslinked composition completely loses its ability to flow. According to the obtained data, the melt flow index (MFI) of the initial PP is 3.12 g/10 min, PP+50 wt% SKN-40+5.0 wt% PPMAA composition is 1.93 g/10min. The introduction of 0.5 wt% of DP in the composition reduces the MFI to 0.55 g/10min, and at the concentration of 1.0 and 2.0 wt% of DP the crosslinked compositions completely lose their ability to flow and the MFI becomes zero. The zero value of MFI does not allow their processing by injection molding and extrusion methods. This is confirmed by the results of evaluation of the gel fraction. According to these data, the introduction of 0.5, 1.0, and 2.0 wt% of DP leads to the formation of gel fractions in the composition, respectively, in an amount of 11, 54 and 78 wt%. The obtained data once again allow us to state that the concentration of the cross-linking agent should be selected experimentally, not exceeding the threshold concentration at which the polymer material loses the ability to be processed on standard equipment for plastics.

Fig. 4 shows the thermomechanical curves of the composition of PP+50wt% SKN-40+5.0wt%

PPMAA+sulphur. The concentration of the vulcanizing agent – sulphur was varied within the range of 3-10 wt%. Analyzing the thermomechanical curves in this figure, you can see that they are radically different from the data shown in Fig.3. The change in sulphur concentration in the range of 3.0, 5.0, 7.0 and 10.0 wt% is accompanied by the formation of high-elastic plateau, characteristic for rubbers. The transition from the crystalline to the high-elastic state takes place at 140, 151, 153, 155 °C, respectively. Along with this, the temperature transition from the high-elastic to the viscous flow state occurs at 173, 175, 180, 198 °C, respectively. Unlike PD, the introduction of sulfur does not lead to the formation of an irreversible highly cross-linked structure, providing the possibility of their processing on the equipment of thermoplastics. The nature of the change in thermomechanical curves is a confirmation of this.

This is confirmed by the results of MFR measuring. So, for example, with an increase in the sulphur concentration from 3 to 10 wt%, the MFR of the samples decreases from 2.76 to 0.616 g/10min.

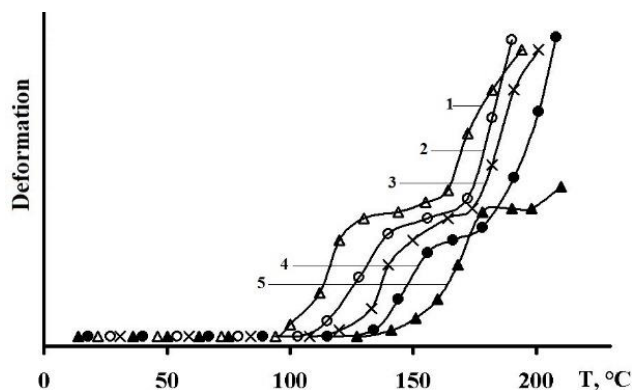


Fig. 4. Influence of the concentration of sulphur (wt %) on the nature of the change in thermomechanical curves of compositions based on PP+50 wt% SKN-40+5 wt% PPMAA+ sulphur: 1- 0; 2- 3.0; 3- 5.0; 4- 7.0; 5- 10.0

Рис. 4. Влияние концентрации серы (%масс.) на характер изменения термомеханических кривых композиций на основе ПП+50%масс. СКН-40+5%масс. ППМАА+сера: 1- 0; 2- 3,0; 3- 5,0; 4- 7,0; 5- 10,0

The process of sulphur vulcanization proceeds mainly through the double bonds present in the polymer matrix. In SKN, the number of double bonds is many times greater than in PP. Therefore, there is reason to believe that sulphur vulcanization will predominantly proceed in the elastomeric phase, allowing dynamically vulcanized thermoplastic elastomers with unique morphological features of the structure, according to which the particles of the cured elastomeric component become dispersed in the continuous thermoplastic matrix of PP.

Thus, on the basis of the foregoing, it can be stated that the study of the thermomechanical properties of the composite materials under consideration makes it possible to obtain rather comprehensive information on the structural features of polymer mixtures and phase transitions from one physical state to an

other. The results of the studies lead to the conclusion that dynamic thermoplastic elastomers are formed not in the course of a simple mixing of a thermoplastic with an elastomer, but as a result of the correct selection of their ratio, the type and concentration of the compatibilizer and the cross-linking agent.

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